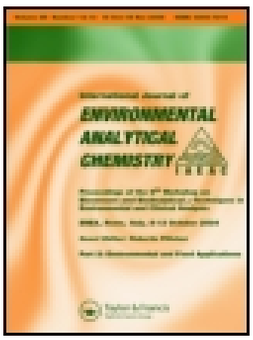

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ARTICLE

Simultaneous ICP-MS determination of trace metals in natural water and snow after their preconcentration on novel adsorbent based on Al_2O_3 impregnated with Alizarin Complexone

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ABSTRACT

A simple and available method for on-line preparation of the adsorbent and solid phase extraction procedure for multi-element determination by inductively coupled plasma mass spectrometry (ICP-MS) has been proposed. The adsorbent (Al_2O_3-PB-AC) was synthesised by sequential impregnation of Al_2O_3 with Polybrene (PB) and Alizarin Complexone (AC). Cd(II), Cr(III), Ni(II), Pb(II) and Zn(II) were quantitatively recovered using Al_2O_3-PB-AC from aqueous solutions at pH 6.5 and at a flow rate of 1.0 mL min^{-1}. All the elements can easily be eluted by 3.0 mL 0.5 M HNO_3. A mini-column packed with 0.100 g Al_2O_3-PB-AC retained all elements quantitatively from up to 50 mL multi-element solution with an enrichment factor of 16.7. The relative standard deviation for five replicate determinations was 3.5%, 7.3%, 6.2%, 7.4% and 4.7% for Cd(II), Cr(III), Ni(II), Pb(II) and Zn(II), respectively, for determination of 5 μg L^{-1} level. The developed method was applied for SPE-ICP-MS determination of Cd, Cr, Ni, Pb, Zn in snow and river waters.

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KEYWORDS
Al_2O_3; Alizarin Complexone; impregnated; preconcentration; multi-element determination; ICP-MS

1. Introduction

Determination of metal ions in various environmental samples such as snow, river and lake samples throughout the year, depending on the time of snow melting or the rainy season, plays an important role in understanding the biogeochemical cycles and the dynamics of fishery waters. Natural waters are polluted by non-ferrous and heavy metals from natural (dust from rocks and surface layers of the soil) and anthropogenic (industrial wastewaters and polluted precipitations) sources. In winter, anthropogenic sources make the main contribution to the pollution of natural objects. The snow cover accumulates pollution from industrial aerosol emissions and car exhaust, so snow is a convenient indicator for assessing the state of pollution. Cd, Cr, Ni, Pb and Zn are widespread industrial pollutants, they can also be part of rocks. The content of these elements in natural waters varies widely depending on geochemical conditions in different seasons [1,2]. Therefore, to understand the sources of pollution of

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natural waters and the level of pollution of the snow cover, it is important to determine the metal content throughout the year.

Inductively coupled plasma mass spectrometry (ICP-MS) is a sensitive multi-element method of analysis that is widely used to determine microelements in the various samples [3–7]. However, when determining metal ions content in natural waters using the ICP-MS

Isotopes	Interferences
^{52}Cr	$^{40}Ar^{12}C$, $^{36}Ar^{16}O$, $^{40}Ca^{12}C$, $^{38}Ar^{14}N$, $^{34}S^{18}O$, $^{35}Cl^{16}OH$
^{53}Cr	$^{40}Ar^{13}C$, $^{37}Cl^{16}O$
^{60}Ni	$^{44}Ca^{16}O$, $^{23}Na^{37}Cl$, $^{24}Mg^{36}Ar$
^{66}Zn	$^{40}Ar^{26}Mg^{+}$, $^{34}S^{16}O_2$
^{67}Zn	$^{35}Cl^{16}O^{16}O$, $^{36}Ar^{31}P$, $^{35}Cl^{32}S$
^{111}Cd	$^{39}K_2{}^{16}O_2H$, $^{95}Mo^{16}O$

method, interference caused by the formation of polyatomic ions of matrix elements of natural waters has a significant influence on the reliability of the obtained results [7,8]:

To eliminate the effect of the interfering overlapping, it makes sense to preconcentrate the analytes and separate them from the matrix components of natural waters using solid phase extraction (SPE) followed by the ICP-MS determination [9]. For the preconcentration of trace elements before their determination, along with chelating resins [10–14], inorganic oxides are the most widely used as adsorbents: silica [15–17], zirconia [18], titania [19], alumina [20,21], as well as composite inorganic materials (core-shell) with a magnetic oxide core [22–24].

Metal oxide adsorbents have several advantages over resins. They are characterised by high mechanical strength of particles, relatively high hydrolytic stability in slightly alkaline and acidic media.

To improve selectivity of inorganic oxides their surfaces are normally modified with various organic complexing reagents, such as N-[2-aminoethyl]-3-aminopropyltrimethoxysilane [25], diphenylcarbazone [26], chromotropic acid [27], 8-hydroxyquinoline [28], 1-(2-pyridylazo)-2-naphthol [29], N-(2-aminoethyl)-2,3-dihydroxybenzaldimine [30], etc. Functional groups are fixed on the surface of inorganic oxides mainly in two ways: non-covalent fixation or impregnation [26–29] or chemical modification [31–33]. The surface arrangement of the functional groups provides good kinetic properties and easy elution of the adsorbed elements.

Non-covalent fixing of organic reagents on the surface of inorganic oxides is easy to implement, does not require complex equipment, various organic solvents and special modifiers. This method of adsorbent preparation differs from chemical modification by fixing complexing agents not due to hard covalent bonds with the surface of inorganic oxides, but due to specific intermolecular interactions.

However, the non-covalent fixing of a wide range of sulpho- or carboxy-derivatives of organic reagents directly on the surface of inorganic oxides is difficult due to the mutual repulsion of negatively charged acid groups of the reagent and deprotonated surface hydroxyl groups. In order to fix sulpho derivatives of organic reagents on the surface of inorganic oxides, its preliminary modification with high molecular weight quaternary ammonium salts [34] or polyhexamethylene guanidine [35,36] is proposed. The amine layer formed on the surface of

the inorganic oxide creates a positive charge on the surface, due to which a sufficiently strong fixation of the sulpho derivatives of organic reagents occurs [37].

Polybrene (hexadimethrine bromide, 1,5-dimethyl-1,5-diazaundecamethelene polymethobromide), which has quaternary amine groups in its molecule, and is capable of producing a polyamine layer on the surface of Al_2O_3, as well as the carboxy derivative of alizarin (Alizarin Complexone) as a reagent, which is capable of producing quite stable complexes with a number of elements [38] were used in this study.

The purpose of the study is to develop a procedure for SPE-ICP-MS determination of Cd(II), Cr(III), Ni(II), Pb(II) and Zn(II) in natural water and snow samples using an adsorbent based on Al_2O_3 sequentially modified with Polybrene and Alizarin Complexone.

2. Experimental

2.1. Reagents and solutions

The standard solutions for making the calibration curves in the ICP-MS measurements were prepared by diluting commercial multielement standard stock solutions (High-Purity Standards, USA) ICP-MCS-1 (for determination of Pb, Cd, Zn) and ICP-MCS-8 (for determination of Cr, Ni). The standard solutions (50 μg L^{-1}) to investigate the recovery of metal ions were prepared by mixing and dilution with 2% (v/v) HNO_3 a single-element National Standard Materials of Russia (Ecoanalytica, Russia) of Cd(II) (№ 7773–2000), Cr(III) (№ 8011–2000), Ni(II) (№ 7785–2000), Pb(II) (№ 7778–2000), and Zn(II) (№ 7770–2000). A 0.8 mM solution of [(3,4-dioxy-2-antrachionyl)methyl] iminodiacetic acid (Alizarin Complexone, AC) purchased from Sigma-Aldrich was prepared by dissolving the exact amount of it in deionised water. A 0.2% (v/v) solution of hexadimethrine bromide (Polybrene, PB) was prepared by dissolving the exact amount of the substance (Sigma-Aldrich) in 0.1 M HCl. Aluminium oxide (particle size of 0.063–0.1 mm, average pore diameter of 25 nm, specific surface area of 93 m^2 g^{-1}) was purchased from Sigma-Aldrich. The required pH of the solutions was adjusted by adding of appropriate amount of HNO_3, NaOH, acetate buffer (0.2 M CH_3COOH and 0.2 M CH_3COONa) for pH 4.0–6.3, bicarbonate buffer (0.2 M $NaHCO_3$ and 0.2 M Na_2CO_3) for pH 6.5–7.5, ammonium buffer (0.1 M NH_3 and 0.1 M NH_4Cl) buffer for pH 8.0. All reagents used were of analytical and spectral purity. Deionised water (18.0 MΩ cm^{-1}) was used to prepare all solutions.

2.2. Apparatus

Inductively coupled plasma mass-spectrometer XSeries II (Thermo Scientific, USA) was used to determine metal ions concentration in solutions. ^{115}In was used as an internal standard. Operational conditions are represented in Table 1. The pH measurements were carried out with a Seven Easy pH Metre S20 (Mettler-Toledo, Switzerland) equipped with InLab Expert Pro pH combination polymer electrode. A multichannel peristaltic pump Boarding longer (Precision Pump Company, China) was used for pumping the solutions through glass mini-column (inner diameter of 3 mm, height of 20 mm) filled with an adsorbent. Deionised water was obtained from E-

Table 1. Operational parameters of mass-spectrometric determination of metals.

Plasma characteristics	
Power of plasma generator	1400 W
CCT	No
Mass detector voltage:	
• Impulse mode	1800 V
• Analogue mode	3300 V
• Standard resolution	83
• Spraying Ar flow	0.94 L min^{-1}
• Cooled Ar flow	13 L min^{-1}
• Ar main stream	0.70 L min^{-1}
Nebuliser	Micromist nebuliser
Spray chamber	Isomist spray chamber cooled at 3°C
Sampling cone	Normal Ni
Skimmer cone	Normal Ni
rpm	25
Spectrometer resolution	Standard
Dwell time	10.0 ms
Separation AMU	0.02
Replicate of measurement	3 times
Elements	Isotopes
Cr	^{52}Cr, ^{53}Cr
Ni	^{60}Ni
Zn	^{66}Zn
Cd	^{111}Cd, ^{112}Cd
Pb	^{207}Pb, ^{208}Pb

pure D 4642–33 (Barnstead International, USA). UV-Vis spectra of AC solutions were registered using Cary 100 spectrophotometer (Varian, Australia). Diffuse reflectance spectra (DRS) of adsorbents were recorded using Pulsar spectrophotocolorimeter (Khimavtomatika, Russia). The spectra are represented in the coordinates *F(R)* – wavelength, nm, where *F(R)* – Kubelka–Munk function.

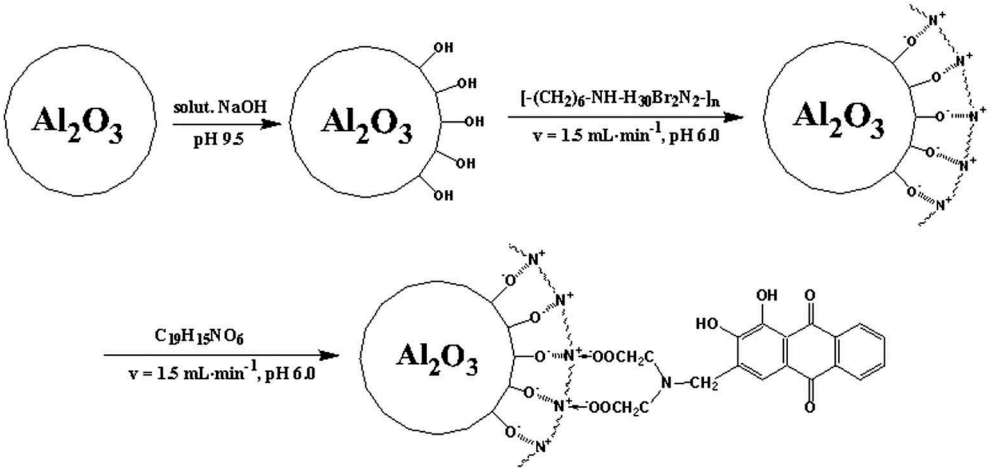
2.3. Adsorbent preparation using the batch technique

In order to activate the surface hydroxyl groups a portion of Al_2O_3 of 10.0 g was soaked with the NaOH solution at pH 9.0–9.5 for an hour and carefully washed by deionised water until neutral pH. Then 100 mL of 0.2% (v/v) PB solution with pH 6.0 was added to activated Al_2O_3 and stirred for an hour. Prepared adsorbent (Al_2O_3-PB) was washed with deionised water until neutral pH reaction of rinsing water. Then, 100 mL of 8.0 mM solution of AC at pH 6.0 was added to Al_2O_3-PB adsorbent and the mixture was stirred for 15 min. Prepared Al_2O_3-PB-AC adsorbent was washed with deionised water and air-dried for 48 hours.

2.4. Preparation the adsorbent in column

A weighed portion of Al2O3 (0.100g) was placed in a mini-column and then 20.0 mL of 0.02% (v/v) PB solution was pumped through it at a flow rate of 1.5 mL min^{-1}. Then, the adsorbent was washed with 10.0 mL of deionised water to remove the excess of PB, followed by passing 10.0 mL of 0.8 mM solution of AC at a flow rate of 1.5 mL min^{-1}. The resulting sorbent was conditioned by passing through a column of 10.0 mL of ammonium acetate buffer mixture with pH 6.5.

The adsorbent synthesis can be described by the following scheme:



2.5. Isotherms of AC adsorption on the Al_2O_3-PB adsorbent

Langmuir and Freundlich adsorption isotherms have been used to characterise the adsorption of AC on the surface of the Al_2O_3-PB adsorbent at the equilibrium. The Langmuir model assumes that adsorption occurs with the formation of a monolayer on the uniform in energy surface when there are no interactions between the adsorbed molecules. This model is described by Equation (1):

$$\frac{C_e}{q_e} = \frac{1}{q_{max} \cdot k_L} + \frac{C_e}{q_{max}} \tag{1}$$

where C_e – concentration of a reagent (mmol L^{-1}) at equilibrium; q_e – amount of the adsorbed reagent at equilibrium (mmol g^{-1}); q_{max} – maximum adsorption capacity for the reagent (mmol g^{-1}); K_L – the Langmuir equilibrium constant (L $mmol^{-1}$). The essential features of the Langmuir isotherm may be expressed in terms of equilibrium parameter R_L, which is a dimensionless constant referred to as separation factor or equilibrium parameter:

$$R_L = \frac{1}{1 + K_L \cdot C_0} \tag{2}$$

where C_0 is the initial concentration of the reagent (mmol L^{-1}), and K_L – the Langmuir equilibrium adsorption constant (L $mmol^{-1}$). R_L value indicates the adsorption nature to be either unfavourable if $R_L > 1$, linear if $R_L = 1$, favourable if $0 < R_L < 1$and irreversible if $R_L = 0$.

The Freundlich model suggests that adsorption occurs on the nonuniform in energy centres and is described by a linear Equation (3):

$$lnq_e = \frac{1}{n} lnC_e + lnK_F \tag{3}$$

where C_e – concentration of the reagent at equilibrium (mmol L^{-1}), q_e – amount of the adsorbed reagent at equilibrium (mmol g^{-1}); K_F – maximum adsorption capacity for the reagent (mmol g^{-1}).

2.6. Elution of Alizarin Complexone

Desorption of AC was studied in the batch conditions. Solutions of NaCl, HCl, and HNO_3 were used as eluents. They were added to 0.100 g of Al_2O_3-PB-AC containing 88 μmol of AC. The mixture was shacked well for 10 min. Then, the solutions were separated and the concentration of AC was determined in them using UV-Vis spectrometry.

2.7. The procedure of separation, preconcentration and elution of metal ions

The adsorption of metal ions was studied in batch and dynamic modes. Effect of the pH of the solution on the solid-phase extraction and adsorption capacity of the adsorbent for Cd(II), Cr(III), Ni(II), Pb(II) and Zn(II) was studied in a batch mode. For this purpose 0.100 g of the Al_2O_3-PB-AC was placed in a test-tube; then, 10.0 mL of a solution containing 50 μg L^{-1} of the metal was added. To adjust the required pH in the range of 1–8, buffer solutions were added into the test tubes. After that, the test tubes were stopped with ground-glass stoppers and shacked well for 15 min.

For determination of adsorption capacity of Al_2O_3-PB-AC for Cd(II), Cr(III), Ni(II), Pb(II), Zn(II) the adsorbent was mixed with 10 mL of solution containing 0.1–100 mg L^{-1} of metal ions with pH 6.5; the mixture was shacked well for 15 min. The distribution of metals was determined via ICP-MS (it needs to be diluted before determination). Adsorption capacity was calculated as follows:

$$q_M = \frac{C_0 - C_e}{m} V$$

where q_M – amount of the adsorbed metal at equilibrium (μmol g^{-1}) C_0 – initial concentration of the metal ions (μmol L^{-1}), C_e – concentration of the metal ion at equilibrium (μmol L^{-1}), m – mass of the adsorbent (g); V – volume of solution (L).

In dynamic experiments 0.100 g of Al_2O_3-PB-AC was placed in a mini-column, then 10.0–200 mL of solution containing 50 μg L^{-1} of Cd(II), Cr(III), Ni(II), Pb(II) or Zn(II) at pH 6.5 and was passed through it at a flow rate of 0.5–3.0 mL min^{-1}. The distribution of metals was controlled using ICP-MS method.

Elution of Cd(II), Cr(III), Ni(II), Pb(II) and Zn(II) was studied in a dynamic mode. After solid-phase extraction of metal ions, 3–10 mL of HNO_3 or HCl solutions with concentration from 0.1 to 1.0 M was passed through a mini-column filled with 0.100 g of Al_2O_3-PB-AC at a flow rate of 1.0 mL min^{-1}.

2.8. Sample preparation

Snow sampling was carried out in the area of the large industrial enterprises of the city, near transport roads in March 2019. A titanium tube (diameter 100 mm) was used for snow sampling. Samples were taken over the entire height of the snow cover, with the prevention of the capture of soil particles from the earth's surface using a polyethylene spade. Such sampling of snow samples eliminates variations (fluctuations in the direction of the wind, inconsistency of emissions) and gives the pollution intensity averaged over a long period of time. Snowmelt water was then filtered through 0.45 mm Millipore

cellulose nitrate membrane to separate suspended particles and the filtrate was acidified to ca. pH 1.7 with 0.2% (v/v) HNO_3.

Samples of river water were taken at the same geolocation point at different times from May 2019 to September 2019 Each water sample was acidified to ca. pH 1.7 with 0.2% (v/v) HNO_3 immediately after sampling. In the laboratory, the samples were filtered through a 0.45 mm Millipore cellulose nitrate membrane to remove particulate matter, then bottled and stored until use.

For analysis, the pH of 100 mL samples (n = 3) of river water and snow samples was adjusted to 6.5 for preconcentration. Samples were passed through mini-column filled with 0.100 g of Al_2O_3-PB-AC adsorbent with the flow rate of 1.0 mL min^{-1}. The desorption of metal ions was carried out using 3 mL of 0.5 M HNO_3.

3. Results and discussion

3.1. Characterisation of the Al_2O_3-PB-AC adsorbent

Extraction of AC from aqueous solutions in the pH range of 3.0–7.0 was 98-99%; time of attainment of adsorption equilibrium was less than 5 min. At pH <3 the extraction of AC was reduced due to protonation of the carboxyl groups of the reagent.

In aqueous solutions AC can exist in four different forms $pK_{1(COOH)} = 2.5$; $pK_{2(COOH)} = 5.8$; $pK_{3(OH)} = 10.0$ and $pK_{4(OH)} = 11.5$ depending on the pH of the solution [39]. During the adsorption of AC in the range of pH 3–8, the surface of Al_2O_3-PB adsorbent turns pink and has a maximum in DRS at 520 nm (Figure 1). Diffuse reflectance spectra of the Al_2O_3-PB-AC adsorbent are identical to the UV-Vis spectrum of the aqueous solution of AC at pH 6.5–9.5 which corresponds to the AC structure with two ionised carboxyl groups. This indicates that fixation of AC on the surface of Al_2O_3-PB proceeds due to the electrostatic interactions between positively charged amine groups of PB and negatively charged carboxyl groups of the AC.

The adsorption capacity of the Al_2O_3-PB adsorbent for AC adsorption calculated from the isotherm of adsorption was found to be 88 μmol g^{-1} (Figure 2). The experimental isotherm of AC adsorption by Al_2O_3-PB has been analysed using the Langmuir and Freundlich models. The value of the K_L factor of the Langmuir model demonstrates a high chemical affinity of the adsorbate to the adsorbent. The value of R_L (separation factor) is $0 < R_L < 1$ proves the favourable adsorption of the AC on the Al_2O_3-PB (Table 2). The plot of C_e/q_e vs. C_e is linear at all range of reagent concentrations, the coefficient of linear correlation being quite high. The adsorption capacity of Al_2O_3-PB for AC calculated by the Langmuir model is 0.089 mmol g^{-1} that comes close to the experimental value.

As one can see from Table 2, the correlation coefficient found for the Freundlich model appeared to be lower than the one for the Langmuir model. The value of the K_F constant, which is in fact the value of the adsorption capacity of the adsorbent, calculated from the Freundlich isotherm appeared to be lower than the value of the experimental adsorption capacity. Therefore, during the modification of the surface of Al_2O_3 with PB all adsorption centres are uniform in energy and the interactions take place only between them and the molecules of AC.

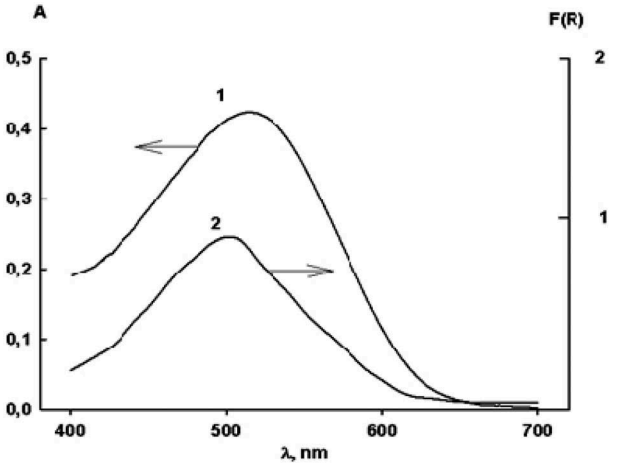


Figure 1. The adsorption spectra of aqueous solutions of AC (1) and DRS of Al_2O_3-PB-AC (2). C_{AC} = 0.26 mM; $V_{solution}$ = 10 mL; $m_{adsorbent}$ = 0.100 g; pH 6.0.

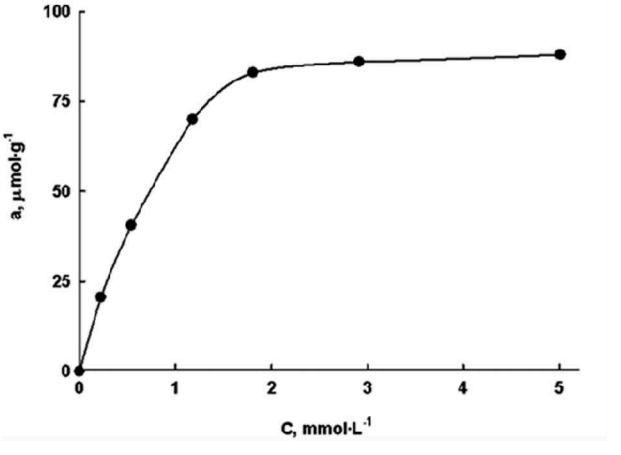


Figure 2. Adsorption isotherm of AC on Al_2O_3-PB at pH 6.0; T = 298 + 5 K; $V_{solution}$ = 10.0 mL; $m_{adsorbent}$ = 0.100 g.

To study the structure of the surface of the proposed adsorbent, FT-IR spectra were registered for the initial Al_2O_3 (Figure 3, spectrum 1); the one modified with PB (Figure 3, spectrum 2); then Al_2O_3 layer-by-layer modified with PB and AC (Figure 3, spectrum 3) and finally the last one is the spectrum of Alizarin Complexone (Figure 3, spectrum 4).

In FT-IR spectrum of Al_2O_3 one can see weak bands in the range of 1800–2400 cm^{-1} which can be attributed to interlayered hydroxyl (OH-) groups connected by relatively strong H-bonds. The intensive bands in the range of 3100–3500 cm-$^{-1}$could be attributed to OH-groups on the surface, i.e. 3500 cm^{-1} is attributed to

Table 2. Langmuir and Freundlich model constants.

Parameters	Langmuir equation
q_{max} (mmol g^{-1})	0.089
k_L (L $mmol^{-1}$)	7.22
R_L	0.027–0.382
R^2	0.9979
	Freundlich equation
K_F (mmol g^{-1})	0.069
n	3.59
1/n	0.2783
R^2	0.9543

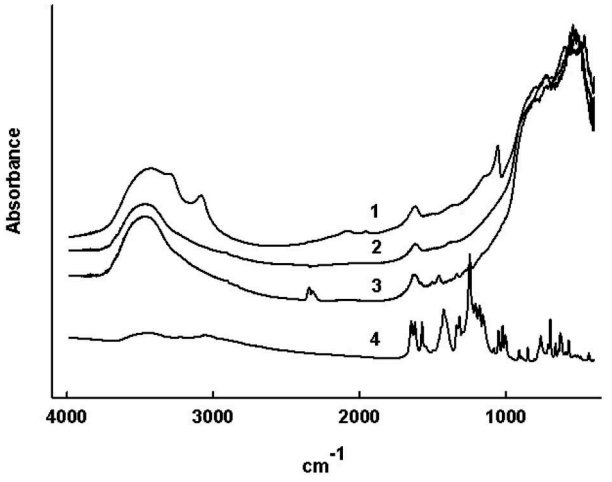
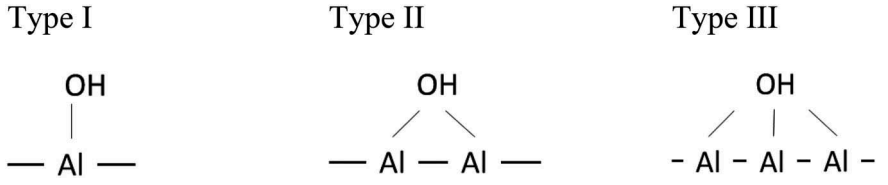


Figure 3. FT-IR-spectra of Al_2O_3 (1), Al_2O_3-PB (2), Al_2O_3-PB-AC (3), Alizarin Complexone (4).



vibrations of type I OH-groups; 3300 cm^{-1} – vibrations of type II OH-groups, and 3100 cm^{-1} – vibrations of type III OH-groups [40]:

In FT-IR spectrum of Al_2O_3-PB-AC new peaks are observed at 1420 cm^{-1} and 1350 cm^{-1} (bending vibrations of -C-N-H-), 1620 cm^{-1} (stretching vibrations of -N-C = C-O-), 2850 cm^{-1} and 2910 cm^{-1} that can be attributed to the saturated -C-H groups [41,42]. Appearance of these frequency bands in FT-IR spectrum of Al_2O_3-PB-AC provides fixation of AC on the surface of Al_2O_3-PB.

Since AC is fixed on the Al_2O_3-PB surface predominantly due to electrostatic interactions, the reagent can be desorbed from the surface of the adsorbent in acidic and highly saline solutions. To study the stability of AC fixation on the surface of Al_2O_3–PB, it was treated with solutions of NaCl, HCl, and HNO_3 and then the degree of desorption of the reagent from the surface was determined. The results presented in Table 3 show that with increasing concentration of acids increases the degree of desorption of AC. The treatment with highly saline solution (up to 100 g L^{-1} NaCl) does not lead to a significant desorption of the organic reagent, that enables the use of the Al_2O_3-PB-AC adsorbent for preconcentration of metal ions from saline water.

3.2. The effect of pH on the preconcentration of metal ions

In the batch mode, Al_2O_3-PB-AC adsorbent extracts Cd(II), Pb(II) and Zn(II); the recovery was more than 98% at the pH 6.0–7.0. In the case of Ni(II) maximum extraction was 97% in the range of pH 7.0–8.0, as for Cr(III) ions it does not exceed 83% (Figure 4). The column procedure allows quantitative extraction of all the ions at pH 6.5 (Table 4).

The extraction of the metal ions takes place due to the formation of complexes with OH-groups of Alizarin Complexone on the Al_2O_3-PB-AC.

Table 3. Desorption (R_{desorb}, %) of Alizarin Complexone from Al_2O_3–PB-AC surface. $m_{adsorbent}$ = 0.100 g; $V_{solution}$ = 10.0 mL; n = 3; P = 0.95.

NaCl, g/L	R_{desorb}, %	HCl, M	R_{desorb}, %	HNO_3, M	R_{desorb}, %
1.00	8.0 ± 0.8	0.1	35.4 ± 0.7	0.1	18.3 ± 0.7
5.00	8.0 ± 0.8	1.0	76.1 ± 0.6	1.0	96.2 ± 0.6
10.0	8.0 ± 0.8	2.0	83.0 ± 0.5	2.0	96.2 ± 0.6
50.0	9.0 ± 0.7	3.0	83.0 ± 0.5	3.0	97.1 ± 0.8
100	11.0 ± 0.7	6.0	83.0 ± 0.6	6.0	97.1 ± 0.5

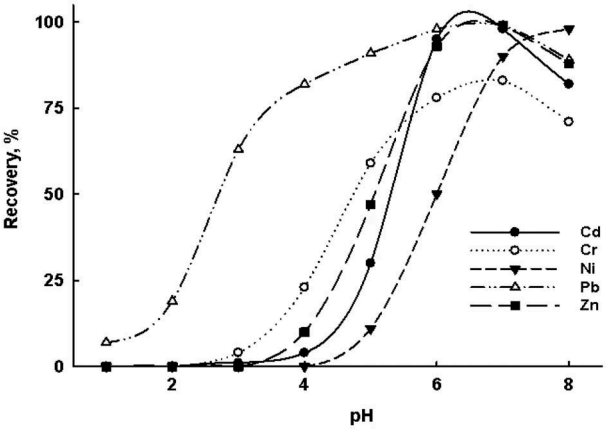


Figure 4. The recovery of Cd(II), Cr(III), Ni(II), Pb(II) and Zn(II) by Al_2O_3-PB-AC vs. pH of solution. C_M = 50 µg L^{-1}; $m_{adorbent}$ = 0.100 g; t = 15 min; $V_{solution}$ = 10.0 mL.

Table 4. The recovery (%) of the metal ions by Al_2O_3-PB-AC in column procedure vs. pH of solution. C_M = 50 μg L^{-1}; $m_{adsorbent}$ = 0.100 g; $V_{solution}$ = 10.0 mL; n = 3; P = 0.95.

Metal ion	pH 6.0	pH 6.5	pH 7.0	pH 7.5
Cd(II)	99.9 ± 0.4	98.9 ± 0.6	97.2 ± 0.5	97.0 ± 0.6
Pb(II)	99.9 ± 0.3	99.9 ± 0.4	98.8 ± 0.8	97.9 ± 0.5
Ni(II)	95.3 ± 0.5	99.6 ± 0.6	98.2 ± 0.6	97.3 ± 0.6
Zn(II)	99.9 ± 0.4	99.9 ± 0.4	98.2 ± 0.6	80.3 ± 0.8
Cr(III)	98.2 ± 0.6	98.7 ± 0.5	92.4 ± 0.7	89.8 ± 0.6

3.3. Adsorption capacity

Adsorption capacity of Al_2O_3-PB-AC with the surface concentration of the reagent of 88 μmol g^{-1} determined from the horizontal section of the adsorption isotherm was: 44 ± 2 for Cd(II), 43 ± 2 for Cr(III), 42 ± 3 for Ni(II), 43 ± 4 for Pb(II) and 41 ± 3 for Zn(II) μmol g^{-1}. A comparison of the amount of adsorbed metal with the surface concentration of the reagent allows us to conclude that stoichiometry of resulting complexes on the surface was M:L = 1:2.

3.4. The effect of the sample volume

To estimate the efficiency of SPE of the metal ions when they are all mixed in a large volume, 200 mL of the solution was passed through a mini-column. At pH 6.5 Zn(II), Pb(II) and Cr(III) were all quantitatively extracted (Figure 5). As for Cd(II) ions, the recovery reduced to 90% when using more than 100 mL of solution. Quantitative extraction of Ni (II) (II) was achieved only by passing of 50 mL; as the volume of the solution increased to 70 mL, the extraction decreased up to 82%. A further increase in the volume of the solution leads to a gradual decrease in the degree of extraction of Ni (II) to 68% as the volume of the solution was 150 mL.

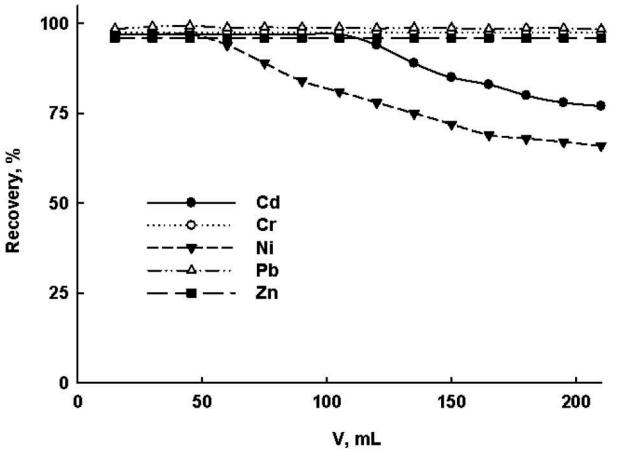


Figure 5. Effect of sample volume on the recovery of Cd(II), Cr(III), Ni(II), Pb(II) and Zn(II) with Al_2O_3-PB-AC packed in mini-column. C_M = 50 μg L^{-1}; $m_{adsorbent}$ = 0.100 g, pH 6.5; flow rate 0.5 mL min^{-1}.

3.5. Effect of the amount of solid phase and the sample flow rate

To optimise the conditions of SPE of elements in a column, the effect of the flow rate and amount of adsorbent on the extraction of metal ions has been studied. The micro-size of Al_2O_3 particles may limit the flow rate of the solution passed through the column and the amount of adsorbent in the column. High flow rates will increase throughput but may lead to loss of analytes due to insufficient time for interaction with the reagent. On the other hand, an increase in the amount of adsorbent in a column leads to an increase in the efficiency of analyte extraction; however, this may decrease the solution flow rate due to the hydrodynamic resistance of the adsorbent microparticles. Therefore, the right choice of the ratio of the amount of solid phase and the flow rate is important to ensure the quantitative extraction of analytes and the optimal throughput of the column.

In studying the effect of the amount of adsorbent, we used 0.050, 0.100, 0.150, 0.200 and 0.300 g portions of adsorbent and a flow rate of 0.5 mL min^{-1}. As it follows from Figure 6, 0.100 g of the adsorbent is the minimum amount that provides quantitative extraction of the entire group of analytes. Reducing the mass of the adsorbent to 0.050 g resulted in the loss of the metal ions. Portions of 0.150 and 0.200 g of sorbent do not provide significant advantages compared to 0.100 g.; Therefore, in further experiments, a portion of 0.100 g of the Al_2O_3-PB-AC adsorbent was used.

The flow rate of the solution was studied in the range of 0.5–3 mL min^{-1} when 50.0 mL of the multi-element solution with a concentration of 50 µg L^{-1} of the metal ion at pH 6.5 was passed through the mini-column. As indicated in Figure 7, the maximum flow rate should not exceed 1 mL min^{-1} in order all the metal ions were quantitatively recovered. In the case of Cd(II), Cr(III), Pb(II), and Zn(II) the flow rate of the solution could be increased up to 2 mL min^{-1}, the degree of the recovery being from 95% (Zn) to 99,5% (Pb). The value of the extraction of Ni(II) is not more than 84% under the test conditions.

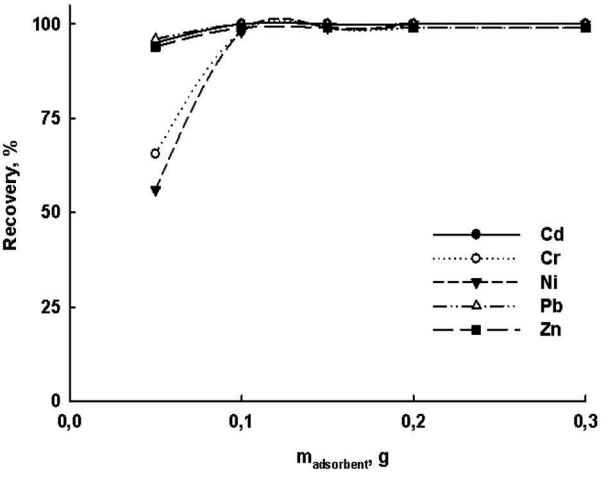


Figure 6. The recovery of Cd(II), Cr(III), Ni(II), Pb(II) and Zn(II) wth Al_2O_3-PB-AC mini-column vs. mass of the adsorbent. C_M = 50 µg L^{-1}; $V_{solution}$ = 50.0 mL; pH = 6.5; flow rate 0.5 mL min^{-1}.

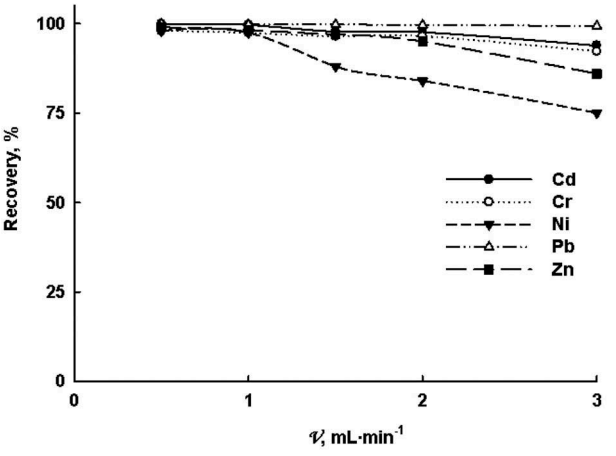


Figure 7. The recovery of Cd(II), Cr(III), Ni(II), Pb(II) and Zn(II) vs. flow rate of the solution. C_M = 50 µg L^{-1}; $m_{adsorbent}$ = 0.100 g; $V_{solution}$ = 50.0 mL; pH = 6.5.

3.6. The effect of the eluent concentration and volume

The ICP-MS determination of elements suggests their quantitative elution from the surface of the adsorbent. Since the extraction of metal ions at pH <3 was not observed (Zn, Cd, Ni) or was insignificant (Pb, Cr), it was proposed to use acidic solutions as eluents of these metals. HNO_3 and HCl solutions with concentration from 0.1 to 1.0 M were studied as potential eluents. With increasing acid concentration from 0.1 to 0.5 M, the elution of elements also increased. The nature of acid used and its volume did not affect the recovery of the ions. Quantitative desorption of metal ions was achieved when 3 mL of 0.5 M HNO_3 or HCl was passed through a mini-column (Table 5). When using 50 mL of the initial solution and 3 mL of the desorbing solution, the preconcentration factor was 16.7.

3.7. Effect of coexisting ions

Since Na^+, K^+, Ca^{2+}, Mg^{2+}, Al^{3+}, Cu^{2+}, SO_4^{2-}, NO_3^-, Cl^-, are the principal components of natural waters, their effect on the SPE of 0.100 mg L^{-1} Cd(II), Cr(III), Ni(II), Pb(II) and Zn(II) from a 50 mL solution under optimum conditions of the preconcentration and subsequent ICP-MS determination have been studied. The tolerance limits of the coexisting ions were considered to be the concentrations at which the recovery of the metal ions in the mini-column experiments was at least 95%.

Table 5. The elution (%) of the metal ions from the Al_2O_3-PB-AC surface in column procedure vs. HNO_3 concentration: $m_{adsorbent}$ = 0.100 g; n = 3; P = 0.95.

$CHNO_3$, M (V, mL)							
				0.5		1.0	
Metal ion	0.1 (5.0)	0.2 (5.0)	0.3 (5.0)	(3.0)	(5.0)	(3.0)	(5.0)
Ni(II)	84.0 ± 0.6	90.7 ± 0.6	96.3 ± 0.5	99.9 ± 0.4	99.9 ± 0.5	99.9 ± 0.5	99.9 ± 0.4
Zn(II)	70.1 ± 0.7	70.2 ± 0.6	99.1 ± 0.5	99.9 ± 0.5	99.9 ± 0.6	99.9 ± 0.5	99.9 ± 0.5
Cd(II)	76.4 ± 0.8	82.8 ± 0.5	83.1 ± 0.6	99.9 ± 0.5	99.9 ± 0.4	99.9 ± 0.6	99.9 ± 0.4
Pb(II)	66.6 ± 0.7	73.7 ± 0.7	83.8 ± 0.7	99.9 ± 0.4	99.9 ± 0.5	99.9 ± 0.4	99.9 ± 0.4
Cr(III)	65.7 ± 0.7	81.8 ± 0.7	99.1 ± 0.5	99.6 ± 0.6	99.7 ± 0.7	99.6 ± 0.6	99.8 ± 0.5

The tolerance limits of the coexisting ions were found to be 50 mg L^{-1} for SO_4^{2-}, NO_3^-, Cl^-, 100 mg L^{-1} for Na^+, K^+, Ca^{2+}, Mg^{2+} and 2 mg·L^{-1} for Al^{3+}, Fe^{3+}, Cu^{2+}. The results show that the added cations and anions did not significantly affect the SPE of the analytes. Therefore, the proposed method can be used to determine Cd(II), Cr(III), Ni(II), Pb(II) and Zn(II) in environmental samples.

3.8. Column lifetime

To study the column lifetime, the mini-column containing 0.100 g of Al_2O_3-PB-AC was put through a number of successive trials:

- modification of Al_2O_3-PB adsorbent with the Alizarin Complexone at a flow rate of the solution of 1.5 mL min^{-1} at pH 6.0;
- adsorption of 50 μg L^{-1} of Cd(II), Cr(III), Ni(II), Pb(II) and Zn(II) from the 50.0 mL of solution at a flow rate of 1 mL min^{-1};
- elution of the ions by 3.0 mL of 0.5 M HNO_3;
- washing the column with 50 mL of deionised water.

Since during desorption of the elements by HNO_3 solutions the substantial desorption of the reagent takes place (see Table 3), the Al_2O_3-PB adsorbent had to be treated the AC solution before the adsorbent was used again to adsorb the elements in the flow analysis. After 15 repeated cycles of metal ions adsorption-desorption with subsequent adsorbent regeneration there was no obvious decrease in the adsorption capacity of the Al_2O_3-PB adsorbent for the AC and metal ions. There was also no changes in the conditions of the SPE of metal ions by the adsorbent and their subsequent ICP-MS determination. Although the reagent was partially desorbed during elution, its concentration in the eluate does not exceed 0.05 M and does not interfere with the ICP-MS determination of the metals.

3.9. Analytical performance

The limit of detection (LOD) of the method using the mini-column filled with Al_2O_3-PB-AC adsorbent was determined under optimal conditions. The LOD was evaluated here as the ratio of three times the standard deviation of 10 blank readings taking into account the preconcentration factor. The LOD was found to be 0.1, 5, 1, 5 and 20 ng·L^{-1} for Cd(II), Cr(III), Ni(II), Pb(II) and Zn(II), respectively.

The relative standard deviations calculated for five replicated adsorption-desorption cycles when determining 5 μg L^{-1} in desorbing solution were found to be 3.5%, 7.3%, 6.2%, 7.4% and 4.7% for Cd(II), Cr(III), Ni(II), Pb(II) and Zn(II), respectively.

3.10. Application of the method

The developed method was applied for ICP-MS determination of Cd, Cr, Ni, Pb, Zn in snow (Table 6) and in river waters (Table 7). Snow sampling was made in the area of Krasnoyarsk

Table 6. The results of Cd(II), Cr(III), Ni(II), Zn(II) and Pb(II) determination in snow samples using the mini-column filled with Al_2O_3-PB-AC: n = 5, P = 0.95.

	Added, μg L^{-1}	Found, μg L^{-1} (Recovery,%)	Added, μg L^{-1}	Found, μg L^{-1} (Recovery,%)	Added, μg L^{-1}	Found, μg L^{-1} (Recovery,%)	Added, μg L^{-1}	Found, μg L^{-1} (Recovery,%)	Added, μg L^{-1}	Found, μg L^{-1} (Recovery,%)
Element	Sample 1		Sample2		Sample 3		Sample 4		Sample 5	
Cd(II)	-	0.064 ± 0.003	-	0.42 ± 0.01	-	0.39 ± 0.01	-	6.3 ± 0.2	-	0.58 ± 0.02
	0.05	0.113 ± 0.005 (99.1)	0.5	0.91 ± 0.03 (98.9)	0.5	0.88 ± 0.03 (98.9)	5.0	11.5 ± 0.4 (101.8)	0.5	1.07 ± 0.04 (99.1)
Cr(III)	-	0.044 ± 0.003	-	2.3 ± 0.1	-	0.19 ± 0.01	-	12.3 ± 0.2	-	11.0 ± 0.7
	0.05	0.096 ± 0.006 (102.1)	2.0	4.2 ± 0.3 (97.7)	0.2	0.39 ± 0.03 (100.0)	10.0	22.5 ± 1.1 (100.9)	10.0	21.3 ± 1.0 (101.4)
Ni(II)	-	0.32 ± 0.01	-	3.4 ± 0.1	-	3.9 ± 0.2	-	7.7 ± 0.3	-	6.5 ± 0.3
	0.2	0.53 ± 0.02 (101.9)	5.0	8.4 ± 0.4 (100.0)	5.0	9.0 ± 0.4 (101.1)	5.0	12.9 ± 0.6 (101.6)	5.0	11.4 ± 0.6 (99.1)
Zn(II)	-	5.2 ± 0.2	-	38 ± 1	-	15.7 ± 0.6	-	75 ± 3*	-	47 ± 2*
	5.0	10.0 ± 0.5 (98.0)	30.0	67 ± 2 (98.5)	5.0	21.0 ± 0.9 (101.4)	30.0	105 ± 4* (100.0)	30.0	79 ± 3* (102.5)
Pb(II)	-	0.24 ± 0.02	-	3.6 ± 0.2	-	1.08 ± 0.06	-	8.2 ± 0.3	-	7.4 ± 0.4
	0.2	0.43 ± 0.03 (97.7)	5.0	8.5 ± 0.4 (99.3)	5.0	6.1 ± 0.4 (100.3)	5.0	13.3 ± 0.4 (100.8)	5.0	12.4 ± 0.5 (100.0)

* – Zn was determined after preconcentration from 10 mL of sample.

Table 7. Determination of Zn(II) and Pb(II) ions in natural waters using the mini-column filled with Al_2O_3-PB-AC: n = 5; P = 0.95.

	Added, μg L^{-1}	Found, μg L^{-1} (Recovery,%)	Added, μg L^{-1}	Found, μg L^{-1} (Recovery,%)	Added, μg L^{-1}	Found, μg L^{-1} (Recovery,%)	Added, μg L^{-1}	Found, μg L^{-1} (Recovery,%)	Added, μg L^{-1}	Found, μg L^{-1} (Recovery,%)
Element	2 May 2019		18 May 2019		16 Juny 2019		15 July 2019		9 September 2019	
					River Yenisei					
Cd(II)	-	0.025 ± 0.001	-	0.0161 ± 0.0005	-	0.023 ± 0.001	-	< LOD	-	0.098 ± 0.003
	0.05	0.074 ± 0.002 (98.7)	0.05	0.066 ± 0.002 (99.8)	0.05	0.073 ± 0.002 (100.0)			0.05	0.149 ± 0.004 (100.6)
Ni(II)	-	0.86 ± 0.05	-	0.71 ± 0.04	-	0.74 ± 0.04	-	0.77 ± 0.05	-	0.80 ± 0.05
	0.5	1.35 ± 0.08 (99.2)	0.5	1.24 ± 0.07 (102.5)	0.5	1.23 ± 0.07 (99.2)	0.5	1.25 ± 0.07 (98.4)	0.5	1.33 ± 0.08 (102.3)
Zn(II)	-	21 ± 1	-	1.26 ± 0.06	-	2.2 ± 0.1	-	5.2 ± 0.2	-	10.2 ± 0.4
	10.0	32 ± 1 (103.2)	3.0	4.3 ± 0.2 (100.9)	3.0	5.1 ± 0.2 (98.1)	3.0	8.2 ± 0.3 (100.0)	10.0	20.5 ± 0.8 (101.5)
Pb(II)	-	1.31 ± 0.09	-	0.13 ± 0.02	-	0.19 ± 0.01	-	0.33 ± 0.02	-	2.2 ± 0.2
	1.0	2.3 ± 0.1 (99.6)	0.5	0.62 ± 0.03 (98.4)	0.5	0.68 ± 0.04 (98.5)	0.5	0.84 ± 0.05 (101.2)	1.0	3.3 ± 0.2 (103.1)
					River Dubches					
Cr(III)	-	0.44 ± 0.03	-	< LOD		< LOD	-	0.27 ± 0.02	-	0.39 ± 0.03
	0.5	0.95 ± 0.07 (101.1)					0.5	0.75 ± 0.05 (97.4)	0.5	0.90 ± 0.07 (101.1)
Ni(II)	-	1.8 ± 0.1	-	1.34 ± 0.08	-	1.19 ± 0.07	-	1.61 ± 0.09	-	1.7 ± 0.1
	1.0	2.8 ± 0.2 (100.0)	1.0	2.4 ± 0.1 (102.6)	1.0	2.2 ± 0.1 (100.5)	1.0	2.6 ± 0.2 (99.6)	1.0	2.7 ± 0.2 (100.0)
Zn(II)	-	40 ± 2	-	3.2 ± 0.1	-	3.0 ± 0.1	-	0.64 ± 0.03	-	22 ± 1
	10.0	52 ± 2 (104.0)	3.0	6.2 ± 0.3 (100.0)	3.0	6.1 ± 0.3 (101.7)	3.0	3.6 ± 0.2 (98.9)	10.0	32 ± 2 (100.0)
Pb(II)	-	2.4 ± 0.2	-	0.26 ± 0.02	-	0.28 ± 0.02	-	0.22 ± 0.02	-	2.0 ± 0.2
	1.0	3.2 ± 0.2 (94.1)	0.5	0.75 ± 0.05 (98.7)	0.5	0.76 ± 0.05 (97.4)	0.5	0.72 ± 0.04 (100.0)	1.0	2.9 ± 0.2 (96.7)

* Concentration of Cr in river Yenisei and Cd in river Dubches below LOD.

city. Sample 1 – snow was collected in an area located far from industrial enterprises and at a distance of 500 m from the road in the park of the university campus. This snow sample was considered by us as a blank. Sample 2 was picked at a road in the city suburb, Sample 3 – at a distance of 100 m from the road in an open area, Sample 4 was picked in the area of the Gulidov Krasnoyarsk Non-Ferrous Metals Plant, Sample 5 – near the oil refinery.

As it follows from Table 6, the area of Krasnoyarsk Non-Ferrous Metals Plant is the mostly contaminated with heavy metals. The excessive amount of heavy metals in snow picked by the road could be caused by mighty exhausts from the city transport. The least pollution with heavy metals was observed in the park zone.

A water sample was taken from the Dubches River (the left tributary of the Yenisei River in the north of the Krasnoyarsk Territory) and the Yenisei River in the central region of the Krasnoyarsk Territory. Samples were taken and prepared using the method described in the Sample Preparation section. The results obtained are presented in Table 7. The correctness of the results was confirmed by the method of 'added-found'. The concentration of metal ions in river samples in summer is much lower than in the spring and autumn. This is due to the fact that in the north of the Krasnoyarsk Territory the end of May – the beginning of June is a period of spring floods. At this time, river waters are significantly diluted with floodwaters, which leads to a sharp decrease in the concentration of dissolved elements. Similar results were obtained by the authors of [2] when studying Siberian rivers.

The analytical performance of the developed method was compared with other known methods (Table 8). The table shows that the LOD of our proposed method is not worse than methods using other adsorbents. It should be noted that when using solid phase extraction, LOD will depend on the preconcentration factor (PF). LOD of elements decreases in proportion to an increase in the ratio of sample volume to eluent volume used for desorption.

In ICP-MS determination of heavy metals in natural waters, the main interference is the formation of polyatomic ions that affect the results. The proposed adsorbent does not extract alkali and alkaline earth metals in the studied pH range, which eliminates the effect of the formation of polyatomic ions.

4. Conclusions

A simple synthesis of the adsorbent based on Al_2O_3 which was modified layer-by-layer with Polybrene and Alizarin Complexone and having a high adsorption capacity for Zn(II), Cd(II), Cr(III), Ni(II) and Pb(II) has been proposed. The adsorbent allows to preconcentrate the group of these metal ions from natural waters for their subsequent mass-spectrometric determination. The developed SPE-ICP-MS procedure comprises of SPE of metal ions using mini-column, elution and subsequent ICP-MS determination of metal ions in eluate. Al_2O_3-PB-AC adsorbent has quiet good stability and allows to use it in at least 15 repeated cycles of metal ions adsorption-desorption without losing its properties.

Table 8. Comparison date of analytical performance of the preconcentration methods for MS-ISP determination of elements in water samples.

Adsorbent	Elements	LOD, ng L^{-1}	RSD, %	PF	Adsorption capacity	Ref.
Chromosorb 106-TAR – 4-(2-thiazolylazo) resorcinol	Cu, Ni, Pb, Zn, Cd	12, 6.4, 21, 15, 1.6	0.3–6.0	5	82-319 μmol g^{-1}	[9]
Ti-containing mesoporous silica	Cr(III), Cu, Cd, Pb	19, 39, 7, 13	7.3, 7.2, 6.8, 6.1	10	3.4–4.7 mg g^{-1}	[15]
L-cysteine functionalised silica	V, Cr(VI), Cu, As(V), Cd, Pb	1.8, 3.7, 2.6, 2.7, 2.1, 3.2	2.5, 4.1, 3.7, 1.9, 3.1, 2.7	86-123	-	[16]
Ion imprinted polymer [Ni(II)-DEM-8-HQ]	Ni, Cu, Pb, Zn	2.2, 6.5, 4.0, 9.0	5.0–6.0	100	-	[43]
NH_2-HCMSSs	Pb, Cd, Zn	21, 4, 7	7.4, 6.2, 5.4	33.3	-	[44]
Al_2O_3-PB-AC	Cd, Cr(III), Ni, Pb, Zn	0.1, 5, 1, 5, 20	3.5, 7.3, 6.2, 7.4, 4.7	16.7	41-44 μmol g^{-1}	This work

Highlights

- Al_2O_3 layer-by-layer modified with Polybrene and Alizarin Complexone was proposed.
- Mini-column filled with adsorbent was used for preconcentration in dynamic mode.
- Al_2O_3-PB-AC separates of Zn, Cd, Cr, Ni, Pb from other metal ions.
- The method was applied in natural waters and snow samples.

Disclosure statement

No potential conflict of interest was reported by the author(s).

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